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Organic Aerosol Formation Downwind from the Deepwater Horizon Oil Spill

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A large fraction of atmospheric aerosols are derived from organic compounds with various volatilities. A National Oceanic and Atmospheric Administration (NOAA) WP-3D research aircraft made airborne measurements of the gaseous and aerosol composition of air over the Deepwater Horizon (DWH) oil spill in the Gulf of Mexico that occurred from April to August 2010. A narrow plume of hydrocarbons was observed downwind of DWH that is attributed to the evaporation of fresh oil on the sea surface. A much wider plume with high concentrations of organic aerosol (>25 micrograms per cubic meter) was attributed to the formation of secondary organic aerosol (SOA) from unmeasured, less volatile hydrocarbons that were emitted from a wider area around DWH. These observations provide direct and compelling evidence for the importance of formation of SOA from less volatile hydrocarbons.

On 20 April 2010, the Deepwater Horizon (DWH) offshore drilling unit exploded, causing the riser pipe to rupture and crude oil to flow into the Gulf of Mexico from a depth of ~1500 m. The oil leak rate was estimated to be 68,000 barrels per day (1), and much of that

oil accumulated on the sea surface. A NOAA WP-3D research aircraft equipped with a large number of instruments to characterize trace gases and aerosols (2) performed two flights near DWH on 8 and 10 June to explore the atmospheric impacts of the spilled oil and of the cleanup activities near DWH. This report discusses one of those impacts: the formation of large concentrations of secondary organic aerosol (SOA) observed downwind from the oil spill. These findings have implications for our general understanding of organic aerosol, which is a large but poorly understood class of atmospheric aerosol

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that affects air quality and climate change (3). A parallel analysis of data from the flights over the oil spill focused on the quantification of atmospheric emissions in general, on the air-water partitioning of volatile organic compounds (VOCs), and on an estimate of the oil leak rate (4).

A large fraction of aerosol in the atmosphere consists of organic material (5). In the polluted atmosphere, the dominant fraction of this organic aerosol (OA) is secondary (6): It is formed in the atmosphere from gas-phase species. Recent research has indicated that SOA formation in polluted air is much more efficient than expected from the measured VOCs [volatile is defined here as having an effective saturation concentration, C^* , of $>10^6 \mu\text{g m}^{-3}$ (7)] and from their particulate mass yields as determined in the laboratory (8–11). One potential explanation for this discrepancy is the formation of SOA from semi-volatile organic compounds (SVOCs; $C^* = 10^{-1}$ to $10^3 \mu\text{g m}^{-3}$) or organic compounds of intermediate volatility (IVOCs; $C^* = 10^3$ to $10^6 \mu\text{g m}^{-3}$) (7, 12). Because SVOCs and IVOCs are typically co-emitted with VOCs, this mechanism has not been unambiguously observed in the atmosphere. As a result, it is currently unknown how much of the discrepancy between measured and expected SOA can be attributed to formation from SVOCs and IVOCs. The oil spill provided a unique environment to study SOA formation from VOCs and IVOCs separately, because organic compounds were released from different parts of the oil slick depending on their volatility.

During both flights over the oil slick, a narrow plume of VOCs and a much wider plume of OA were observed downwind of DWH (Fig. 1). Results from the 10 June 2010 flight are discussed here in detail, as higher and more constant wind speeds on this day led to a more easily interpretable data set. The extent of the surface oil slick on 10 June (Fig. 1) is estimated from a composite of multiple satellite instruments (13). VOCs and OA were not enhanced everywhere over the oil but were instead confined to much narrower plumes downwind of DWH. Data from two periods (defined in Fig. 1C) are further examined in Fig. 2. Period P1 represents the measurements made closest to DWH; period P2 was farthest from DWH.

The evaporation of freshly surfaced oil was the dominant source of the VOCs measured downwind of DWH (4). In laboratory analyses of oil spilled at DWH (14), the first 23% of the mass evaporated within 2 hours (fig. S1). During a 2-hour period, the sea surface transport of oil is a few kilometers at most, which explains why the VOCs were emitted from only a small area and confined to a narrow plume (Fig. 1C). As described elsewhere in detail (4), the composition of VOCs measured in canister samples collected in the plumes was dominated by alkanes and aromatics. The relative abundance of the VOCs measured in the atmosphere reflected the composition of the spilled oil itself, with the exception of a subset of lighter VOCs that dissolved

either completely or partially during transport from the sea bottom to the surface. Other sources of VOCs (e.g., from ships and flares) were much smaller and had a different VOC composition; burning of surface oil did not occur on 10 June.

A plume of OA was observed downwind of DWH (Fig. 1B), with mass loadings peaking at $>25 \mu\text{g m}^{-3}$ on 8 June and $>10 \mu\text{g m}^{-3}$ on 10 June; these values are in the range of OA observed in U.S. urban atmospheres (5). Because the measured OA was not correlated with tracers of incomplete combustion, such as black carbon aerosol and carbon monoxide (Fig. 2), we can rule out a combustion-related source. For reasons outlined below, we argue that the OA was largely formed from vapors released from the oil and the condensation of their atmospheric oxidation products onto existing particles. First, the mass flux of OA increased with distance downwind of DWH. Second, measured particle number size distributions indicated a growth in particle size

downwind of DWH (Fig. 2B). This rules out wave-generated emission of aerosol from the sea surface—a known source of aerosol in marine air (15)—as the dominant source of OA in this case, because it would have led to the same particle sizes at all downwind distances. Total particle number concentrations, not shown here, remained relatively constant between periods P1 and P2, which, together with the observed increase in aerosol mass (Fig. 2A), rules out coagulation as the primary cause of the growth in particle size.

One further observation regarding the OA is noted here but not explored in detail. Mass spectral analysis of the aerosol (5) indicates that both oxygenated organic aerosol (OOA) and hydrocarbon-like organic aerosol (HOA) increased in the aerosol downwind, with a larger contribution from HOA than from OOA (Fig. 2A). Although HOA and OOA are typically

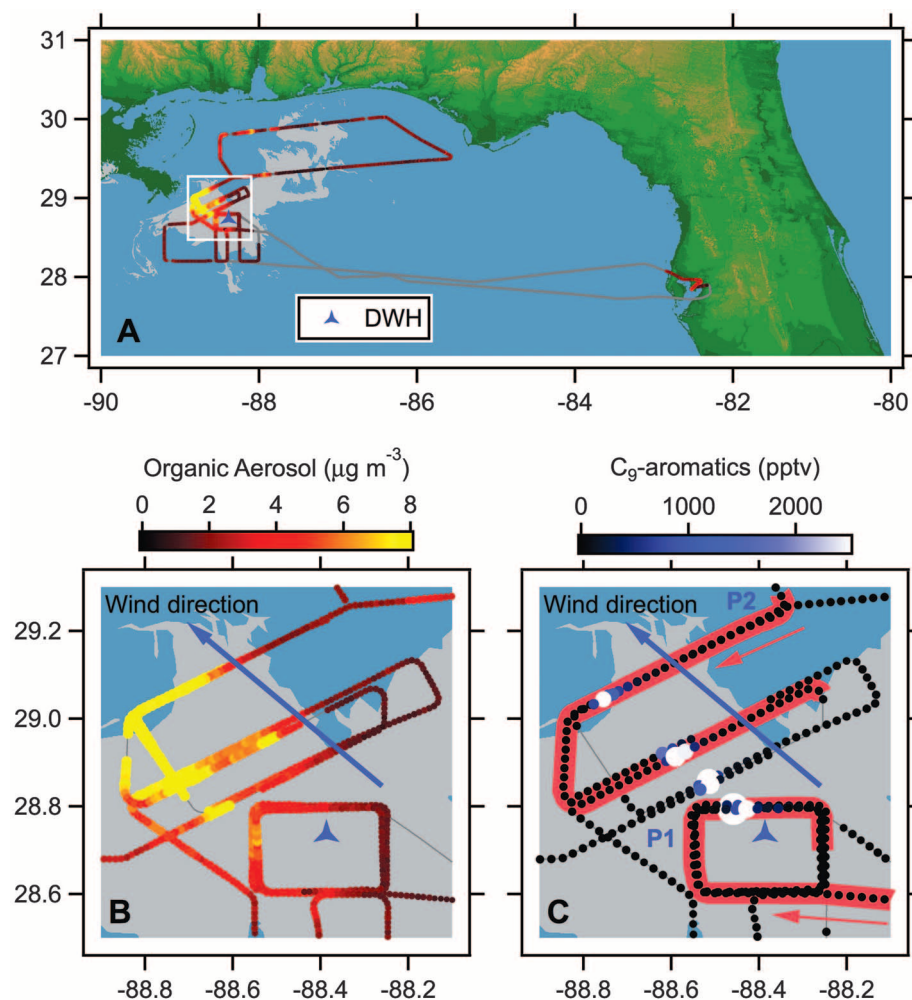


Fig. 1. (A) Flight track on 10 June 2010, with data points below 900 m color- and size-coded by the measured concentration of organic aerosol. The gray area underlying the flight track represents the extent of the oil slick derived from multiple satellite observations. (B and C) The area indicated by the white square in (A) is shown in more detail in (B) and color- and size-coded by the measured C_9 -aromatics in (C). Data from the periods P1 and P2, indicated in red in (C) with arrows indicating the flight direction, are shown in more detail in Fig. 2. Degrees latitude and longitude are indicated along the y and x axes, respectively.

attributed to direct emission from combustion sources and to secondary formation, respectively, our results show that HOA can also be formed in the atmosphere.

Aromatics and C_8 to C_{11} alkanes are known to be SOA precursors (16, 17) and were measured at very high mixing ratios downwind of DWH (Fig. 1C), higher than typically observed in urban areas (18, 19). However, the SOA was not primarily formed from these VOCs, because the observed OA plume was much wider than the VOC plume and because VOCs were not enhanced upwind from the OA plume. Instead, we argue here that IVOCs evaporating from the oil were the SOA precursors. As their evaporation is

slower, these species were transported on the sea surface away from the area where the spilled oil surfaced and were released to the atmosphere from a wider area (Fig. 3A). Further evidence for this conceptual model is obtained from the plume widths of the measured VOCs, whose vapor pressures span about two orders of magnitude. Figure 3B shows that close to DWH, the width of the VOC plume increased with the molecular weight of the VOC.

SOA was not additionally enhanced in the narrow VOC plume despite very high mixing ratios of precursors. Calculations with the Weather Research and Forecasting model coupled with Chemistry (WRF-Chem) indicates that the very

high VOC mixing ratios combined with moderately enhanced NO_x (1 to 5 parts per billion by volume) resulted in low concentrations of hydroxyl radicals in the narrow VOC plume. Therefore, only a small fraction of the measured VOCs reacted to form SOA in the downwind distance sampled by the aircraft.

What were the precursors of the SOA formed downwind of DWH? We constructed a volatility distribution of the oil (Fig. 4A)—that is, the mass fraction as a function of the effective saturation concentration C^* (7)—using the hydrocarbon composition of the spilled oil (4) and assuming that the value of C^* for a hydrocarbon is the same as that for an n -alkane with the same number of carbon atoms (fig. S2). Assuming that the evaporation rate of a compound is proportional to its vapor pressure, we can fit the measured evaporation curve for the spilled oil (fig. S1) using the volatility distribution (Fig. 4A) and one free parameter, A , that equates the evaporation rate of each volatility class to $A \times C^*$. The best fit, shown by the envelope of contributions from all volatility classes in Fig. 4B, suggests that for $C^* \geq 10^8 \mu g m^{-3}$ ($\leq C_8$ hydrocarbons), evaporation takes <1 hour. For $C^* = 10^4$ to $10^7 \mu g m^{-3}$ (C_9 to C_{18} hydrocarbons), evaporation takes place on time scales varying from 1 to 1000 hours. For $C^* \leq 10^3 \mu g m^{-3}$ ($\geq C_{19}$ hydrocarbons), evaporation takes >1000 hours.

To relate the time scales for evaporation of the precursor VOCs to spatial scales, we used an offline Lagrangian particle transport model to simulate surface oil trajectories on the basis of hourly seawater velocity data from the Naval Research Laboratory's HYCOM-based 0.04° Gulf of Mexico Ocean Prediction system (20, 21). In the model, 1000 to 5000 particles representing freshly surfaced oil were released within an area of 4 km by 4 km, and their spreading on the sea surface due to advection, wind drift, and parameterized subgrid scale diffusion was described. From the time since surfacing, the model calculates the area where emissions to the atmosphere occur for species with evaporation lifetimes of 1 to 1000 hours, respectively (Fig. 4C and fig. S3). In the model, compounds that evaporate in <10 hours are released to the atmosphere from a small area near DWH, whereas compounds that evaporate in >100 hours are released from an area that is much larger than the extent of the OA plume. We conclude that the compounds responsible for SOA formation were most likely released on evaporation time scales of 10 to 100 hours. The best fit to the evaporation curve in Fig. 4B suggests that on these time scales, evaporation is dominated by $C^* = 10^5 \mu g m^{-3}$ compounds (C_{14} to C_{16} hydrocarbons), and we conclude that these species were the most likely precursors of the observed SOA. The effective saturation concentration (C^*) equals the ambient mass loading at which partitioning of a compound shifts between the gas and condensed phases; a C^* value of $10^5 \mu g m^{-3}$ is much higher than ambient mass loading ($\sim 10 \mu g m^{-3}$),

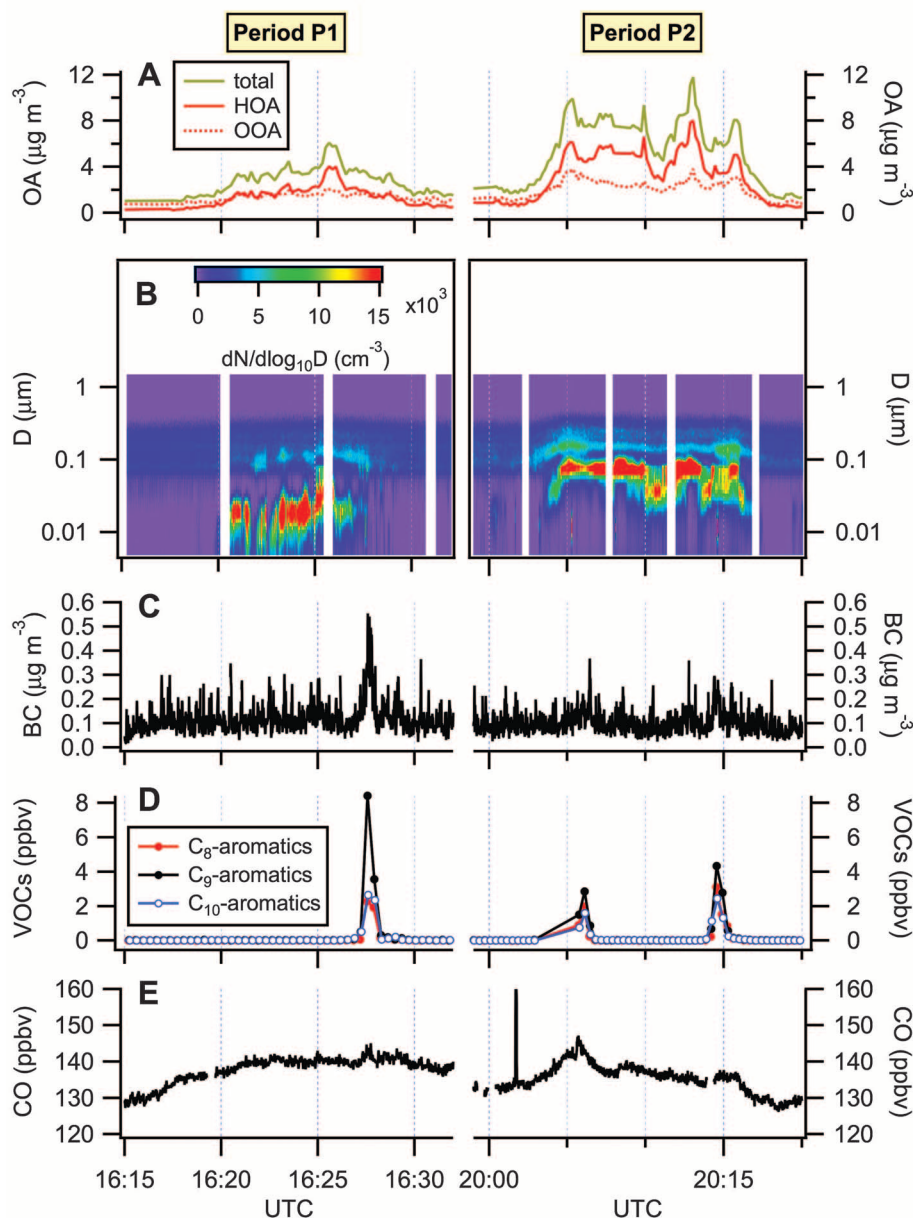


Fig. 2. Time series of selected data from periods P1 and P2 (Fig. 1): (A) organic aerosol and its contributions from hydrocarbon-like organic aerosol (HOA) and oxygenated organic aerosol (OOA), (B) particle number size distributions, (C) black carbon (BC) aerosol, (D) aromatic volatile organic compounds (VOCs), and (E) carbon monoxide (CO).

Fig. 3. (A) Conceptual model describing the observations of VOCs and organic aerosol downwind from the oil spill. Oil from the leaking riser pipe surfaces in a relatively small area. The most volatile fraction of the oil evaporates within hours, leading to a narrow atmospheric plume of VOCs downwind from the spill site. The less volatile fraction takes longer to evaporate, during which time the oil spreads over a larger area. Organic aerosol is formed from the less volatile fraction and is observed in a wider plume downwind. **(B)** Measurements of different aromatic species shortly downwind from the oil spill demonstrate that the plume broadens as a function of decreasing volatility, in accordance with the conceptual model. Mixing ratios were normalized to their maximum value during this transect to facilitate the comparison of plume shapes.

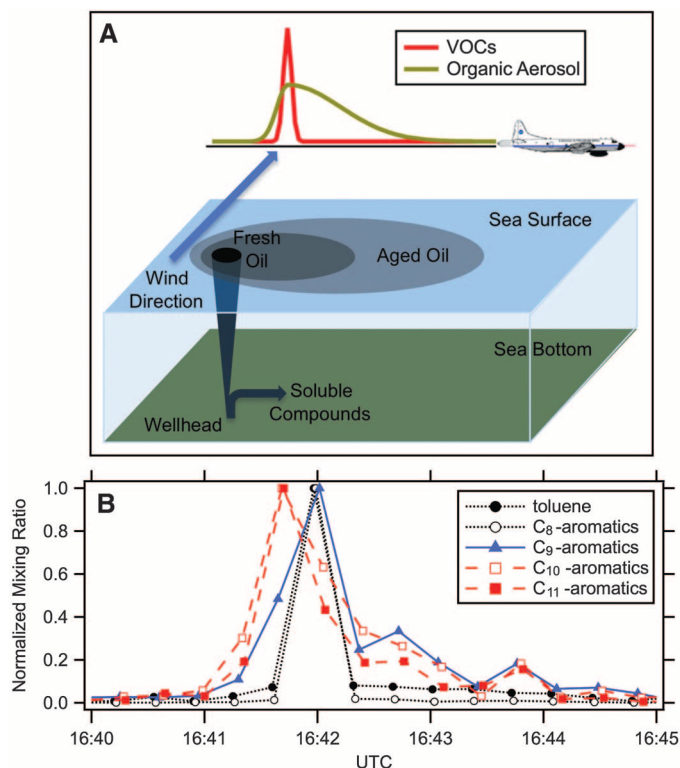
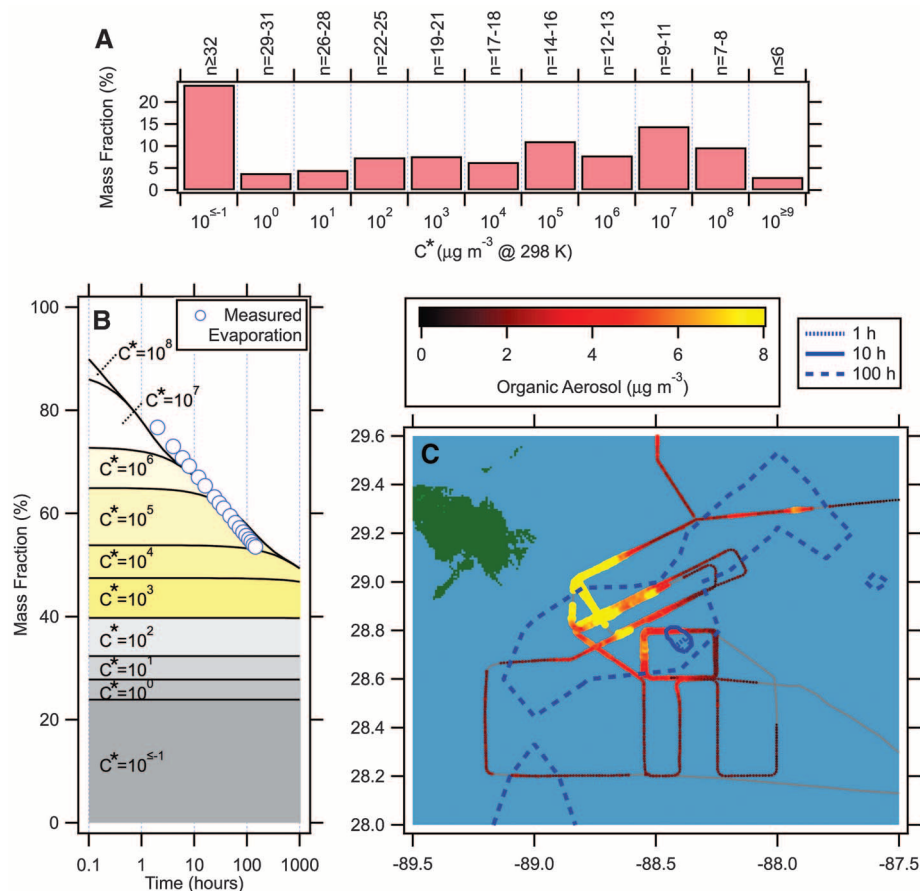


Fig. 4. (A) Volatility distribution of oil spilled at DWH derived from the oil composition. The numbers on the top axis indicate the number of carbon atoms of the corresponding hydrocarbons. **(B)** Evaporation of oil as a function of time (blue circles) (14) fit using the volatility distribution from (A). **(C)** Modeled distribution of a compound that surfaces at the DWH spill site and evaporates with a mean lifetime of 1, 10, and 100 hours, respectively. The blue curves outline the areas where concentrations are $\geq 10\%$ of the maximum value. The flight track on 10 June 2010, color-coded by the measured concentration of organic aerosol, is added for comparison.



which suggests that a substantial chemical transformation of these hydrocarbon precursors must take place to lower their volatility and produce SOA. On the basis of the distance of the downwind transect P2 (Fig. 1C) to the DWH spill site (45 km) and the average wind speed (5 m s⁻¹), we estimate that this chemical transformation occurred in <3 hours.

How efficient was SOA formation from $C^* = 10^5 \mu\text{g m}^{-3}$ compounds over the oil? The total leak rate of oil from DWH on 10 June was estimated to be $2.03 \times 10^6 \text{ kg day}^{-1}$ (4). Of this total, 11% ($2.2 \times 10^5 \text{ kg day}^{-1}$) is estimated to be in the $C^* = 10^5 \mu\text{g m}^{-3}$ class (Fig. 4A). The flux of OA farthest downwind of DWH (estimated from the integral of the measured concentration times orthogonal wind speed and multiplied by the depth of the boundary layer) (4, 22) was $8 \times 10^4 \text{ kg day}^{-1}$, which may be a lower estimate because the aircraft did not sample across the full width of the SOA plume (Fig. 1B). From these numbers, we estimate the SOA yield for $C^* = 10^5 \mu\text{g m}^{-3}$ compounds to be $\sim 36\%$, in approximate agreement with laboratory studies (12).

Previous work has suggested that SOA formation from SVOCs and IVOCs could be an important source of aerosol in the United States (12). However, field verification of this chemistry has been difficult because SVOCs and IVOCs are typically co-emitted with VOCs; for that

reason, the SOA observed in polluted air cannot be unambiguously attributed to formation from SVOCs and IVOCs. The DWH oil spill provided a unique look at this chemistry because the emissions of VOCs, IVOCs, and SVOCs were spatially separated and the importance of SOA formation from IVOCs could be clearly demonstrated. These results form a well-constrained case to improve our quantitative understanding of IVOC chemistry, which will help to describe the importance of IVOCs for SOA formation in other polluted regions of the atmosphere.

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Supporting Online Material

www.sciencemag.org/cgi/content/full/331/6022/1295/DC1

Materials and Methods

Figs. S1 to S3

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